PATENT SPECIFICATION

NO DRAWINGS

857,174

Date of Application and filing Complete Specification April 23, 1959.

No. 13835/59.

Application made in United States of America on Aug. 22, 1958.

Complete Specification Published Dec. 29, 1960.

Index at acceptance: —Classes 95, B4(B:X); and 140, A(2H: 2L:2N3:2N6:4:5G6:11F:13:16B3:17).

International Classification: —B05. B29d.

COMPLETE SPECIFICATION

Laminated Glass Products

We, THE GOODYEAR TIRE & RUBBER COMPANY, a corporation organized under the laws of the State of Ohio, United States of America, with offices at 1144, East Market Street, Akron, Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to laminated products.

According to this invention, laminated products are produced by forming a composite product of at least one layer or sheet of glass and at least one layer of a random ethylene terephthalate-ethylene isophthalate copolyester in which the ethylene terephthalate units comprise from 85% to 30% of the sum of the ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units correspondingly comprise from 15% to 70% of said sum.

The polyesters used in this invention are linear random copolyesters formed by the condensation of terephthalic acid and isophthalic acid or ester-forming derivatives of these acids with ethylene glycol. They are conveniently prepared by the method shown in British Patent 766,290 published January 16, 1957, in which a mixture of dimethyl terephthalate and dimethyl isophthalate is subjected to ester interchange reaction with ethylene glycol in the presence of an ester interchange catalyst and then the bis ethylene glycol esters or low polymers thereof are condensed, with the elimination of glycol, to form high molecular weight linear polyesters. For preparing the laminates, polyesters having an ethylene terephthalate-ethylene isophthalate ratio of from 85/15 to 30/70 can be used. Ordinarily, and particularly for the preparation of safety glass, copolyesters are used in which the ethylene terephthalate units comprise from 75 to 30% of the sum of the ethylene terephthalate and ethylene isophthalate units, and the ethylene isophthalate units comprise from 25 to 70% of said sum. Preferred resins for use in safety glass are the resins in which the ethylene terephthalate units comprise from 75 to 50% of the sum of the ethylene terephthalate and ethylene isophthalate units and the ethylene isophthalate units comprise correspondingly from 25 to 50% of said sum. Still more preferred are the resins in which the ethylene terephthalate units comprise from 75 to 60% of the sum of the ethylene terephthalate and ethylene isophthalate units and the ethylene isophthalate units comprise correspondingly from 25 to 40% of said sum. The most preferred resins for use in making glass laminates are the amorphous resins in which the ethylene terephthalate units comprise from 65 to 30 percent of the sum of the ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units comprise from 35 to 70 percent of said sum.

Copolyesters of the invention in which the ethylene terephthalate units comprise 65 percent or more of the ester units in the copolyester are crystallizable. In order that they be free from haziness or cloudiness they should be amorphous and should not substantially crystallize. As the proportion of ethylene terephthalate increases, the rate of crystallization and the total amount of crystallization obtainable increase. Copolyesters containing from 85 to 65 percent of ethylene terephthalate units have relatively slow rates of crystallization and do not substantially crystallize unless they are heated at temperatures above their minimum crystallization temperature for considerable periods of time. Thus, the copolyester containing 65 percent of ethylene terephthalate has a much slower rate of crystallization than does the copolyester containing 85 percent of ethylene terephthalate units. Copolyesters of this invention in which the ethylene terephthalate units comprise from 65

[*Price 3s. 6d.*]

Price 75c

Price 25

to 30 percent of the ester units in the copolyester are substantially non-crystallizable and remain completely or substantially amorphous. They are the preferred copolyesters for use in the present invention.

The various copolyesters of the invention can readily be prepared by the method of the British Patent, 766,290, by suitably adjusting the proportions of the starting materials used.

The copolyesters used for preparing the glass laminates are used as amorphous materials. They can be applied as self-supporting films, in which case a pre-formed film of an ethylene terephthalate-ethylene isophthalate copolyester resin such as, for example, a resin in which the ethylene terephthalate units comprise from 65 to 30% of the sum of the ethylene terephthalate and ethylene isophthalate units and the ethylene isophthalate units correspondingly comprise from 35 to 70% of said sum is placed between sheets of glass, the composite structure is heated at a temperature above the sticking temperature of the film and then cooled. Preferably, the composite article is heated to a temperature just above the second order transition temperature of the resin, subjected to light pressure of from 10 pounds per square inch to 50 pounds per square inch, then the temperature is raised to a temperature above the softening or sticking temperature of the resin, the pressure is increased to from 50 to 500 pounds per square inch and the composite article formed is cooled.

The pressure used in preparing the laminates can be varied over a wide range. Generally, the pressure will not be above 500 pounds per square inch. The temperature range in the first stage is a temperature in the range of from 60 to 80° C. which is just above the second order transition temperature of the resin. In the second stage the temperature range as used is above the softening or sticking temperature of the film. Generally in this stage a temperature in the range of from 125 to 170° C. is used.

Pressure can be applied by any suitable means. For example, a press, pressure rolls, C-clamps or other methods well-known in the art can be used.

Another method of preparing the laminates comprises coating at least one side of a sheet of glass with the copolyester, superimposing another sheet of glass on the coating, heating to a temperature above the second order transition temperature of the copolyester and pressing and then further heating at a temperature above the softening or sticking temperature of the film while pressing and then cooling the composite article. Laminates can also be made by spreading a solution of the polyester resin on a glass surface and evaporating the solvent to deposit a film of the resin. Another method of forming laminates is to form a film on glass plates by placing a layer of granules of copolyester on the surface of a glass sheet and heating and pressing to fuse the granules and form a film. If desired, another sheet of glass can be placed in contact with the coating or film formed on the glass sheet and the composite article heated and pressed. Still another method of preparing the laminates is to dip a film of the copolyester in a solvent, place the film between two sheets of glass and subject the composite articles to heat and pressure.

Glass laminates having extra strength can be prepared using an oriented film as a reinforcing layer. An amorphous layer of an ethylene terephthalate-ethylene isophthalate copolyester in which the ethylene terephthalate units comprise from 65 to 30 percent of the sum of the ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units correspondingly comprise from 35 to 70 percent of said sum is used as an adhesive or bonding layer between the oriented film and the glass surface. These laminates can be made by coating the glass surface with a solution of the copolyester and evaporating the solvent to deposit an amorphous layer of copolyster on the glass, placing an oriented film in contact with the amorphous copolyester coating on the glass and heating and pressing the composite article to form the laminate. Another method is to place an amorphous film next to the glass surface and an oriented film next to the amorphous film. The article can then be laminated by heating and pressing. Still another method is to coat the oriented film with a coating of amorphous copolyester by a suitable method such as by coating it with a solution of copolyster and evaporating off the solvent. The oriented film thus coated on one or both sides can be laminated to one or, if desired, to two sheets of glass.

The oriented films useful as reinforcing layers in the present invention are oriented films made from copolyesters such as the ethylene terephthalate-ethylene isophthalate copolyesters in which the ethylene terephthalate units comprise from 90 to 70 percent of the sum of the ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units comprise from 10 to 30 percent of said sum. The films are oriented by stretching. One-way stretched film or biaxially oriented films can be used. Films particularly useful for making strong laminated glass products of this invention are biaxially-oriented, heat-set films of these polyesters. Oriented films of polymeric ethylene terephthalate can also be used as well as oriented films of other crystallizable linear polyesters having a high melting point. When an oriented film is used as a reinforcing layer, the temperature used in laminating must be below that at which the oriented film will soften and become disoriented. Thus it is

apparent that the lamination is carried out at a temperature below the melting point of oriented, crystallized or heat-set film used as a reinforcing layer.

The following examples illustrate the practice of the invention, particularly with respect to the preparation of shatter-resistant safety glass.

EXAMPLE 1.

An 0.008 inch thick amorphous film of a 75/25 ethylene terephthalate-ethylene isophthalate copolyester was placed between two sheets of clean double-strength window glass. The glass plates were then placed in a press and warmed to a temperature just above the second order transition temperature (82° C.) of the resin at a pressure of from 10 to 50 pounds per square inch. The temperature of the press was then raised to 121° C., and the pressure was increased to from 50 to 350 pounds per square inch. The press was cooled slightly, and the composite article was removed from the press. A transparent, brilliantly clear laminate resulted. The laminated glass was struck a sharp blow with a hammer. It was very resistant to shattering and splintering.

EXAMPLE 2.

The procedure used in Example 1 was repeated using an amorphous film of a 60/40 ethylene terephthalate-ethylene isophthalate copolyester. This laminated structure was also shatter-resistant and resistant to splintering.

EXAMPLE 3.

Each of two sheets of double-strength window glass was coaaed on one side with a solution of a 60/40 ethylene terephthalate-ethylene isophthalate copolyester, in a 50:50 (by weight) mixture of chloroform and trichloroethane. The solvent was evaporated, leaving a light film or coating of amorphous polyester on the glass surface. A two mill thick biaxially oriented film of a 75/25 ethylene terephthalate-ethylene isophthalate copolyester was placed between the coated surface of the glass sheets and the molding procedure of Example 1 was repeated. A strong shatter-resistant glass laminate was produced.

EXAMPLE 4.

Each of two sheets of glass was coated on one side with a solution of a 60/40 ethylene terephthalate ethylene isophthalate copolyester in a 50:50 (by weight) mixture of chloroform and trichloroethane. The solvent was evaporated leaving a light coating of the polyester on the glass surface. A two mil thick heat-set biaxially oriented film of a 75/25 ethylene terephthalate-ethylene isophthalate copolyester was placed between the coated surfaces of the glass sheets, and the molding procedure of Example 1 was repeated. A strong shatter-resistant glass laminate was produced.

EXAMPLE 5.

Each of two sheets of double strength window glass was coated on one side with a solution of 60/40 ethylene terephthalate-ethylene isophthalate copolyester in a 50:50 (by weight mixture of chloroform and trichloroethane). The solvent was evaporated leaving a light film or coating of the polyester on the glass surface. A 0.002 inch thick amorphous film of a 75/25 ethylene terephthalate-ethylene isophthalate copolyester was placed between the coated surfaces of the glass sheets, and the molding procedure of Example 1 was repeated. A strong shatter-resistant glass laminate was produced.

EXAMPLE 6.

0.002 inch thick amorphous film of a 60/40 ethylene terephthalate-ethylene isophthalate copolyester was dipped in a bath of trichloroethane solvent and soaked for a few seconds. It was then removed from the solvent bath and placed between two sheets of glass, and the sheets were pressed together by means of C-clamps having a plate or sheet of metal between the clamps and the glass to distribute the pressure evenly and to avoid localized high pressure points immediately under the clamps. The clamped sheets were then placed in an oven and heated to a temperature of 93° C., then removed from the oven and cooled. A strong shatter-resistant glass laminate was produced.

EXAMPLE 7.

A 0.012 inch thick amorphous film of a 60/40 ethylene terephthalate-ethylene isophthalate copolyester was dipped in a bath of trichloroethane solvent and soaked for a few seconds. It was then removed from the solvent bath and placed between two sheets of glass, and the sheets were pressed together by means of C-clamps having a plate or sheet of metal between the clamps and the glass to distribute the pressure evenly and to avoid localized high pressure points immediately under the clamps. The clamped sheets were placed in an oven and heated to a temperature of 93° C., and then removed from the oven and cooled. A strong shatter-resistant glass laminate was produced.

The present invention contemplates the production of decorative as well as reinforced articles. The practice of the invention with respect to these types of laminates is illustrated by the following examples:—

EXAMPLE 8.

A film of a 60/40 ethylene terephthalate-ethylene isophthalate copolyester was steeped in a chloroform bath for a few minutes, removed from the bath and heated at 220° F. to cause absorbed chloroform to rapidly evaporate and form bubbles in the film. This foamed film was then placed between two

sheets of glass and the laminate was pressed and heated according to the method of Example 1. The product was a strong shatter-resistant laminate similar in appearance to frosted glass.

EXAMPLE 9.

A 60/40 ethylene terephthalate-ethylene isophthalate copolyester film containing a small amount of bronze powder as a pigment was laminated between two sheets of glass by pressing and heating according to the method of Example 1. The product was a strong shatter-resistant transparent laminate having a light bronze color.

EXAMPLE 10.

A laminated glass structure having a pleasing wood grain appearance was made by laminating a very thin wood veneer between two sheets of glass using a 60/40 ethylene terephthalate-ethylene isophthalate copolyester film between the glass and the wood veneer to laminate the sheets together and heating and pressing as in Example 1. A strong shatter-resistant glass laminate having a pleasing appearance was produced.

The examples illustrate the invention in several if its aspects. The invention provides an easy method of making reinforced and decorative laminates. The films can be clear, foamed, translucent or opaque, or white or colored, e.g., by addition to the film of a dye or white or colored pigment, or by addition of a finely divided metal such as bronze powder, aluminium powder, etc., thus giving a wide range of glass articles. The thickness of the films used in this invention is not critical. A film only thick enough to prevent glass to glass contact can be used or thicker films can be used if desired. As a practical mattter, the films will seldom be thicker than the glass plates being laminated, and will ordinarily be thinner, but films thicker than the glass plates can be used if desired.

The examples have illustrated the invention particularly with respect to glass-film-glass laminates. The invention also contemplates film-glass-film laminates, and articles in which only one side of a sheet or mass of glass is coated with a film of resin. Also, if desired, laminated products having a greater number of layers of film and glass can be made. It has been found that resins with which the invention is concerned have a very great affinity for glass and adhere tenaciously. Thus, a sheet or mass of glass which is coated with a film of a resin of this invention is shatter-resistant and resistant to splintering because the resin reinforces the glass and retains splinters which would otherwise fly from the glass when it is struck a hard blow.

The examples have shown the use of uncompounded films. Plasticizers can be added if desired, and small amounts of other resins or other compounding ingredients can be mixed with the copolyesters used in this invention.

The method of this invention has several advantages over the prior art methods. Some of these advantages are: The invention provides shatter-resistant laminates which can be clear, colored, frosted, or have a design or pattern; simplified production procedures can be used because the invention provides for the use of a film which can be merely inserted between glass plates and heated and pressed; the invention provides laminates having improved optical qualities and improved age resistance; the copolyester films used have very strong adhesion to glass, and this makes the glass shatter-resistant and resistant to splintering.

WHAT WE CLAIM IS:—

1. A method of making a laminated product characterized by contacting at least one surface of a piece of glass with an ethylene terephthalate-ethylene isophthalate copolyester in which the ethylene terephthalate units comprise from 85 to 30% of the sum of the ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units comprise correspondinly from 15 to 70% of said sum placing another piece of glass in contact with the polyester containing surface and heating and pressing and then cooling the product.

2. A method according to Claim 1 in which the ethylene terephthalate units comprise from 75 to 30% of the sum of the ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units comprise correspondingly from 25 to 70% of said sum.

3. A method according to Claim 2 in which the ethylene terephthalate units comprise from 75 to 50% of the sum of the ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units comprise from 25 to 50% of said sum.

4. A method according to Claim 3 in which the ethylene terephthalate units comprise from 75 to 60% of the sum of the ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units comprise correspondinly from 25 to 40% of said sum.

5. A method according to any of Claims 1 to 4 in which the copolyester is in the form of a film and is placed between the two pieces of glass.

6. A method according to Claim 5 in which the film is dipped in a solvent bath and then placed between the two sheets of glass, the sheets subsequently being subjected to compressive force and heated while being compressed, the product then being cooled.

7. A method according to any of Claims 1 to 4 in which the copolyester is coated on

the surface of the glass and another piece of glass is placed in contact with the coated surface, the product being heated, pressed and then cooled.

8. A method according to Claim 7 in which the piece of glass that is placed in contact with the coated surface also has copolyesters coated thereon.

9. A method according to any of Claims 1 to 8 in which the laminate is heated at a temperature above the second order transition temperature of the copolyester and pressed, and then further heated at a temperature above the softening temperature of the copolyester while pressing, the product then being cooled.

10. A method according to Claim 5 in which the film is a foamed film.

11. A method according to any of Claims 1 to 9 in which the copolyester used is colored.

12. A method according to any of Claims 1 to 9 in which the copolyester contains a white pigment.

13. A method according to any of Claims 1 to 9 in which the copolyester contains a powdered metal pigment.

14. A method of making a laminated product characterized by coating a surface of each of two pieces of glass with a coating of an ethylene terephthalate-ethylene isophthalate copolyester in which the ethylene terephthalate units comprise from 65 to 30% of the sum of the ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units correspondingly comprise from 35 to 70% of said sum, placing an oriented film of an ethylene terephthalate-ethylene isophthalate copolyester in which the ethylene terephthalate units comprise from 90 to 70% of the sum of ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units comprise from 10 to 30 percent of said sum between the two coated surfaces and heating and pressing and then cooling the composite article.

15. A method according to Claim 14 in which the film spaced between the two coated glass surfaces is a biaxially oriented film.

16. A method according to Claim 14 in which the film placed between the two coated glass surfaces is a biaxially oriented, heat-set film.

17. A laminated article characterized by at least one layer of glass and at least one layer of an ethylene terephthalate-ethylene isophthalate copolyester in which the ethylene terephthalate units comprise from 85 to 30% of the sum of the ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units correspondingly comprise from 15 to 70% of said sum.

18. A safety glass characterized by at least two layers of glass and as a reinforcing and adhesive layer between them a layer of an ethylene terephthalate-ethylene isophthalate copolyester in which the ethylene terephthalate units comprise from 75 to 30% of the sum of the ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units correspondingly comprise from 25 to 70% of said sum.

19. A laminated article characterized by (a) a layer of glass, (b) an oriented film of an ethylene terephthalate-ethylene isophthalate copolyester in which the ethylene terephthalate units comprise from 90 to 70 percent of the sum of ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units comprise from 10 to 30 percent of said sum and (c) as an adhesive layer between them a layer of an ethylene terephthalate-ethylene isophthalate copolyester in which the ethylene terephthalate units comprise from 85 to 30 percent of the sum of the ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units comprise from 15 to 70 percent of said sum.

20. A laminated product made by the method set forth in Claim 5, in which the copolyester layer comprises an ethylene terephthalate-ethylene isophthalate copolyester in which the ethylene terephthalate units comprise from 75 to 60% of the sum of the ethylene terephthalate and ethylene isophthalate units in the coplyester and the ethylene isophthalate units correspondingly comprise from 25 to 40% of said sum.

21. A method of making a laminated product characterized by coating a surface of each of two pieces of glass with a coating of an ethylene terephthalate-ethylene isophthalate copolyester in which the ethylene terephthalate units comprise from 65 to 30% of the sum of the ethylene terephthalate and ethylene isophthalate units in the copolyester and the ethylene isophthalate units correspondingly comprise from 35 to 70% of said sum, placing an oriented film of a crystallisable linear polyester having a high melting point between the two coated surfaces and heating and pressing and then cooling the composite article.

22. The method according to Claim 21 wherein said crystallisable linear polyester is polymeric ethylene terephthalate.

23. A method of making a laminated product substantially as set forth and described hereinbefore.

24. A method of making a laminated product substantially in accordance with the foregoing examples.

25. A laminated product substantially as set forth and described hereinbefore.

MARKS & CLERK.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1960.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained